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Description

This invention pertains to improved polyester moldings and more particularly to those having improved surface characteristics.

A technical improvement that has made a significant contribution to commercial polyester molding technology is the use of low profile additives to reduce shrinkage during the curing reaction, and to thereby improve dimensional stability and surface smoothness. Low profile additives are thermoplastic polymers such as vinyl acetate polymers, polystyrene, acrylic polymers, and polycaprolactones. There are a number of theories that seek to explain the low profile or anti-shrinkage action of these polymers, but the one that seems to best explain the phenomenon is the following:

The low profile additive is at least partly soluble in the uncured polyester/styrene solution. As the polyester/styrene mixture crosslinks, the thermoplastic polymer becomes incompatible or less soluble and at least partly comes out of solution. This action causes a volume expansion that compensates for the shrinkage that occurs when the polyester/styrene mixture crosslinks.

The development of low-profile unsaturated polyester compounds has led to a wide acceptance of these materials by the transportation industry because of their good surface appearance, dimensional stability, physical properties, assembly consolidation and potential weight savings. However, as new applications developed standards have been raised making it desirable for even better surface appearance and the elimination of ripples and waviness that sometimes develop, particularly in relatively large appearance sensitive areas.

There is, therefore, a need to provide low-profile unsaturated polyester compounds which afford improved surface appearance in the molded parts obtainable therefrom.

In accordance with the invention, it has been found that polyester molding compositions meeting the above-described needs comprise:

- (a) a polyester resin comprising the reaction product of an olefinically unsaturated dicarboxylic acid or anhydride and a polyol;
- (b) an olefinically unsaturated monomer that is copolymerizable with said polyester resin;
- (c) a thermoplastic vinyl acetate polymer low-profile additive to control shrinkage; and
- (d) an effective amount of a secondary cross-linkable vinyl monomer having a reactivity ratio with styrene of greater than 1.

Based on this finding, the invention as claimed has been made.

The polyesters that are employed in the invention include reaction products of a dicarboxylic acid or anhydride, with a polyhydric alcohol. The dicarboxylic acids or anhydrides that are employed to produce the polyester, either singly or in combination, must include those that contain olefinic unsaturation, preferably wherein the olefinic unsaturation is alpha, beta- to at least one of the carboxylic acid groups. Such acids include maleic acid or anhydride, fumaric acid, tetrahydrophthalic acid or anhydride, hexachloroendomethylene tetrahydrophthalic anhydride ("chlorendic anhydride"), Diels-Alder adducts of maleic acid or anhydride with compounds having conjugated olefinic unsaturation, such adducts being exemplified by bicyclo[2.2.1] hept-5-en-3-2,3-dicarboxylic anhydride, methyl maleic acid, and itaconic acid. Maleic acid or anhydride and fumaric acid are the most widely used commercially.

In addition to the olefinically unsaturated acid or anhydride, saturated and/or aromatic dicarboxylic acids or anhydrides can also be employed in producing the polyester. Such acids include phthalic acid or anhydride, terephthalic acid, hexahydrophthalic acid or anhydride, adipic acid, isophthalic acid, and "dimer" acid (i.e., dimerized fatty acids).

In addition to the above esters one may also use dicyclopentadiene modified unsaturated polyester resins described in US-A-3,986,922 and US-A-3,883,612.

A polyol is also employed to produce the polyester. Such polyols include ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, butylene glycols, neopentyl glycol, glycerol and 1,1,1-trimethylolpropane. As a rule, not more than about 20 mole per cent of the polyol will be triol, with the remainder being one or more diols.

Vinyl ester resins that have been advantageously employed in both bulk molding compounds (BMC) and sheet molding compounds (SMC) are resins wherein the secondary hydroxyl group formed by the interaction of an epoxide group with a carboxylic acid group has been reacted with a dicarboxylic acid anhydride to produce pendant carboxylic acid groups. A variety of saturated and unsaturated anhydrides similar to those described as useful in preparing polyester resins may be used in proportions of at least about 0.1 mole of anhydride per equivalent of hydroxyl group up to an amount sufficient to react with each hydroxyl.

Thermosetting resins that are classified herein as vinyl ester resins, which contain the characteristic linkages and terminal, polymerizable unsaturated groups, are fully disclosed in US-A-3,887,515 along with the preparation of such resins.

As is known in the art, polyesters that are employed in thickened molding compositions must contain residual acidity in order to enter into the thickening reaction. The nature and production of the polyesters used in such applications are known in the art.

The polyester composition of the invention also contains a monomer that contains ethylenic unsaturation, and which is copolymerizable with the polyester. Styrene is the preferred monomer in commercial practice today, although others can be used. Such others include vinyl toluene, methyl methacrylate, chlorostyrene, and the like.

The said monomer is employed in the polyester composition for the purpose of dissolving the polyester (which is a solid at ambient temperatures, i.e., about 20°—25°C) to ensure that the polyester composition is a fluid. Enough monomer is employed so that the thickness or viscosity of the fluid is such that the fluid can be processed conveniently. Excessive amounts of the monomer are normally to be avoided, because such excess can have an adverse effect on properties. For instance, too much of the monomer may tend to cause embrittlement of the cured polyester. Within these guidelines, effective proportions of the monomer are normally found within the range of from about 35 to about 70 and preferably 40 to 55, weight percent based on weight of polyester plus monomer, plus low profile additive.

If a thickening agent is also employed in the invention, these materials are known in the art, and include the oxides and hydroxides of the metals of Groups I, II and III of the Periodic Table. Specific illustrative examples of thickening agents include magnesium oxide, calcium oxide, zinc oxide, barium oxide, calcium hydroxide, magnesium hydroxide, mixtures thereof and others known to the art. Thickening agents are normally employed in proportions of from about 0.1 to about 6 weight percent, based upon weight of polyester resin, plus monomer, plus low profile additive.

In one aspect, the invention employs a carboxylated vinyl acetate polymer low profile additive.

Such polymers include copolymers of vinyl acetate and ethylenically unsaturated carboxylic acids such as acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, and the like; vinyl acetate/vinyl chloride/maleic acid terpolymer, and the like. Reference is made to US—A—3,718,714 and GB—A—1,361,841, for descriptions of carboxylated vinyl acetate polymer low profile additives.

The useful carboxylated vinyl acetate polymer low profile additives ordinarily have molecular weights within the range of from about 10,000 to about 250,000, and preferably from about 25,000 to about 175,000. They are usually employed in proportions of from about 6 to 20, and preferably from about 9 to 16, weight percent, based on weight of polyester plus low profile additive, plus monomer.

As a general rule, the solution polymerized carboxylated vinyl acetate polymers are preferred in commercial practice because of their better batch-to-bath uniformity.

Other thermoplastic polymers useful as low profile additives include vinyl acetate homopolymers.

The polyester molding composition may also contain one or more of the known types of conventional additives, which are employed for their known purposes in the usual amounts. The following are illustrative of such additives:

1. Polymerization initiators such as t-butyl hydroperoxide, t-butyl perbenzoate, benzoyl peroxide, cumene hydroperoxide, methyl ethyl ketone peroxide, and others known to the art. The polymerization initiator is employed in a catalytically effective amount, such as from about 0.3 to about 2 to 3 weight percent, based on the weight of polyester plus monomer plus low profile additive;
2. Fillers such as clay, hydrated alumina, silica, calcium carbonate and others known to the art;
3. Reinforcing fillers such as glass fibers or fabrics, asbestos fibers or fabrics, various organic fibers or fabrics such as those made of polypropylene, acrylonitrile/vinyl chloride copolymer, and others known to the art; and
4. Mold release agents or lubricants, such as zinc stearate, calcium stearate, and others known to the art.
5. Rubbers or elastomers such as (a): homopolymers or copolymers of conjugated dienes having a weight average molecular weight of 30,000 to 400,000 or higher as described in US—A—4,020,036. The conjugated dienes contain from 4—12 carbon atoms per molecule such as 1,3-butadiene, isoprene, and the like; (b) epihalohydrin homopolymers, a copolymer of two or more epihalohydrin monomer(s), or a copolymer of an epihalohydrin monomer(s) with an oxide monomer(s) having a number average molecular weight (M_n) which varies from about 800 to about 50,000 as described in US—A—4,101,604; (c) chloroprene polymers including homopolymers of chloroprene and copolymers of chloroprene with sulfur and/or with at least one copolymerizable organic monomer wherein chloroprene constitutes at least 50 weight percent of the organic monomer make-up of the copolymer as described in US—A—4,161,471; (d) hydrocarbon polymers including ethylene/propylene dipolymers and copolymers of ethylene/propylene and at least one nonconjugated diene, such as ethylene/propylene/hexadiene terpolymers and ethylene/propylene/1,4-hexadiene/norbomadiene, as described in US—A—4,161,471; (e) conjugated diene butyl elastomers, such as copolymers consisting of from 85 to 99.5% by weight of a C_4 — C_7 isolefin combined with 15 to 0.5% by

weight of a conjugated multi-olefin having 4 to 14 carbon atoms, copolymers of isobutylene and isoprene where a major portion of the isoprene units combined therein have conjugated diene unsaturation as described in US—A—4,160,759.

The polyester molding compositions of the invention can be cured under conditions similar to those used for known polyester compositions. Typical curing conditions are a temperature of from about 93 to 177°C (200° to 350°F) for 1 to 4 minutes at a pressure of 20.7 to 138 bar (300 to 2000 psi).

Although relatively low levels, that is one to about six parts of secondary crosslinkable monomer per hundred of the total composition of polyester resin, thermoplastic polymer and monomer, are effective in producing molded parts with better surface appearance than heretofore available, somewhat larger amounts can be used if desired, i.e., up to about 10 parts per hundred. Above this level, however, surface characteristics of molded parts are inferior to those using a monomer such as styrene alone.

The secondary crosslinkable monomer suitable for use in the present invention has a reactivity ratio with styrene of greater than 1, preferably greater than 5, and most preferably greater than 20.

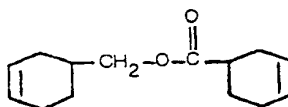
Measuring the reactivity ratios of monomers is well known in the art as described, for example, in F. W. Billmeyer, Jr., *Textbook of Polymer Science*, Wiley-Interscience, pages 329-331.

The monomer reactivity ratios r_1 and r_2 are the ratios of the rate constant for a given radical adding its own monomer to that for its adding the other monomer. Thus $r_1 > 1$ means that the radical M_1 prefers to add M_1 ; $r_1 < 1$ means that it prefers to add M_2 . In the system styrene (M_1)-methyl methacrylate (M_2), for example, $r_1 = 0.52$ and $r_2 = 0.46$; each radical adds the other monomer about twice as fast as its own. Thus, methyl methacrylate is unsatisfactory in the molding compositions of this invention.

The following Table lists representative styrene-monomer reactivity ratios.

	Monomer-1	Monomer-2	r_1	r_2
25	Styrene	Diethylfumarate	0.30	0.07
		Diethylfumarate	0.400	0.0905
		Methyl methacrylate	0.52	0.46
30		Methyl methacrylate	0.59	0.536
		Vinyl acetate	55	0.01
		Vinyl methyl ether	100	0.01
35		Vinyl ethyl ether	90	0
		Vinyl nonanoate	49.5	0.01
		Vinyl octadecanoate	68	0.01
40		Vinyl stearate	68	0.01
		Vinyl undecanoate	29	0.02
		Allyl acetate	90	0.00
45		Diallylphthalate	328	0.057
		Diethyl maleate	6.52	0.005
		Ethyl 2-ethoxyacrylate	23.5	~0
50		Vinyl trimethoxysilane	22	0

Other monomers suitable for use in this invention include vinyl norbornene, vinyl stearate, butyl vinyl ether, diallyl phthalate, octene-1, octene-2, vinyl cyclohexene, bicyclononadiene, dicyclopentadiene, and the following:



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The invention is further described in the examples which follow. All parts and percentages are by weight unless otherwise specified.

10 In formulating the compositions of this invention which are to be used in molding applications including both sheet molding and bulk molding, it is customary to admix with the unsaturated polyesters and the low-profile additives the following materials:

1. A polymerizable ethylenically unsaturated monomer which serves to crosslink the unsaturated polyester to a thermoset product.
2. A peroxide which serves to accelerate the cross-linking reaction.
- 15 3. A thickening agent which serves to provide body to the compositions by increasing the viscosity of the polyester.
4. Fillers, including fillers which serve as reinforcing agents such as glassfibers and the like.

The compositions of this invention can be prepared by mixing the components in a suitable apparatus such as a Hobart mixer, at temperatures in the order of about 20°C to about 50°C. The components may be combined 20 in any convenient order. Generally, it is preferable that the thermosetting resin and low-profile additive are added in liquid form by preparing a solution thereof in styrene or other liquid copolymerizable monomer. All the liquid components are usually mixed together including the crosslinkable vinyl monomers of this invention before adding the fillers and thickening agent. Once formulated, the compositions can be molded into thermoset articles of desired shape, particularly thermoset articles such as automobile fenders, dash-boards and the like. 25 The actual molding cycle will, of course, depend upon the exact composition being molded as well as upon the nature of a particular cured product desired. Suitable moldings cycles are conducted at temperatures of the order of about 100°C to about 182°C for periods of time ranging from about 0.5 minutes to about 5 minutes. The shrinkage data molding conditions for making 30.5x30.5x0.32 cm (12"x12"x.1/8") plaques were two minutes at 148°C and 55.2 bar (800 psi) unless otherwise.

30 The molding viscosities were measured on paste samples containing all of the ingredients except the fiberglass using a Brookfield HBT 5x Viscometer TF spindle at 5 rpm.

Experimental section

35 General procedure for preparation of bulk molding compound (BMC) formulations

All the liquid components were weighed individually into a Hobart mixing pan placed on a Toledo balance. The pan was attached to a Model C-100 Hobart mixer (in a hood). The agitator was started at slow speed, then increased to medium speed to completely mix the liquids over a period of 3—5 minutes. The agitator was then 40 stopped and the internal mold release agent was next added to the liquid from an ice cream carton. The Hobart mixer was restarted and the mold release agent mixed with the liquid until it was completely wet out. The filler was next added to the pan contents (agitator off) then mixed, using medium to high speed, until a consistent paste was obtained. The mixer was again stopped and the weighed amount of thickening agent was mixed into the paste over a period of 2—3 minutes, the mixer was again stopped and ~175 grams of the paste were 45 removed from the pan (using a large spatula) and transferred to a wide-mouthed 113.4 g (4 oz.) bottle. This paste sample was stored in the capped bottle at room temperature and the viscosity was measured periodically using a Model HBT 5x Brookfield Synchro-Lectric Viscometer on a Helipath Stand.

After removal of the paste sample, the contents were reweighed and styrene loss made up, the chopped glass fibers were added slowly (from an ice cream carton) to the pan with the mixer running on slow speed. 50 The mixer was run for ~30 seconds after all the glass was in the paste. This short time gave glass wet out without glass degradation. The pan was then removed from the mixer and separate portions of the BMC mix of ~450 grams each were removed using spatulas and transferred to aluminum foil lying on a balance pan (balance in the hood). The mix was tightly wrapped in the aluminum foil (to prevent loss of styrene via evaporation) and stored at room temperature until the viscosity of the retained paste sample reached molding viscosity. 55 The weight of the BMC added to the foil varies with the molding application.

General procedure for preparation of sheet molding compound (SMC) formulations

All the liquid components were weighed individually into a 18.9 liter (5 gallon) open top container placed on a Toledo balance. The contents of the container were then mixed (in a hood) with a high speed Cowles type dissolver. The agitator was started at a slow speed, then increased to medium speed to completely mix the liquids over a period of 2—3 minutes. The mold release agent, if one is desired, was next added to the liquids from an ice cream carton and mixed until completely dispersed. The filler was next added gradually from a tared container until a consistent paste was obtained and the contents were then further mixed to a minimum temperature of 32°C (90°F). The thickener was next mixed into the paste over a period of 2—3 minutes, the mixer was stopped and ~175 grams of the paste was removed from the container and transferred to a wide-mouthed 113.4 g (4 oz.) bottle. The paste sample was stored in the capped bottle at room temperature and the viscosity measured periodically using a Model HBT 5x Brookfield Synchro-Lectric Viscometer on a Helipath Stand.

The balance of the paste is next added to the doctor boxes on the SMC machine where it is further combined with fiber glass (~2.54 cm (1") fibers). The sheet molding compound (SMC) is then allowed to mature to molding viscosity and then molded into the desired article.

Molding facilities

30.5x30.5x0.32 cm (12"x 12"x 1/8") test panels Flat panels for MCR surface evaluation are molded on a 75 TON Queens Hydraulic press. The press contains a matched dye set of 30.5x 30.5 cm (12"x 12") chrome plated molds. The female cavity is installed in the bottom and the male portion is at the top. Both molds are electrically heated and are controlled on separate circuits so that the molds can be operated at different temperatures. For our molding the top and bottom temperature was 149°C (300°F). The molding pressure which can be varied from 0—75 TON was run at maximum pressure. The molds do not contain ejector pins; therefore, the molded panel is removed with a rubber suction cup and the use of a stream of air. The panels are laid on a flat surface, weighted to keep them flat and allowed to cool overnight. The molded panel is measured with a micro caliper from corner to corner in all four directions to determine shrinkage which is an average of the four readings. These panels are also used for surface smoothness determinations with the Bendix Profilometer.

Hood scoops

Hood Scoops designed like miniature automobile hoods and containing a number of ribs and bosses of varying sizes was used to determine "sink", surface smoothness and overall moldability of sheet molding compound formulations containing surface improvers. The hood scoop contains a large triangular boss (~4.8 cm (1.9") base ~9.7 cm (3.8") high) and 3 circular bosses (~1 cm (0.4"), ~2.3 cm (0.9"), ~3.6 cm (1.4") diameter). It also contains a number of ribs of varying thickness and with different lead in radii.

Visual observations of these hood scoops as molded and after painting with a gloss black paint enables one to compare "sink" over the ribs and bosses, craze cracking, surface smoothness, glass pattern, laking and overall moldability. The hood scoop mold is installed in a 200 Ton Lawton hydraulic press. The molds contain ejector pins for release of the molded part and are heated with circulating oil. The male core is installed in the bottom of the press and the female cavity at the top. Temperatures of the two molds are controlled separately. Pressure of the press can be varied up to 200 Ton with variable time cycles so that the same part can be molded at several pressures. The speed at which the press closes can also be varied as well as the cure cycle for the molded part. All of these were varied during the molding of SMC formulations containing the surface improvers. Placement of the change pattern on the male core mold was also varied. The molded hood scoop was allowed to cool and was then evaluated.

Transfer molding press—Tree mold

The molding press used is a 100 ton hydraulic press with an 45.7x30.5 cm (18"x 12") platen area. The press contains a tree mold. The tree mold has a number of cavities of varying length, shapes, and thickness. In molding the part a 180 g charge of sheet molding compound (SMC) or bulk molding compound (BMC) is added to the ram port. The ram piston which has an adjustable pressure range of 0—138 bar (2000 psi) then pushes the charge into the tree mold cavities where it is cured. The gate sizes going into each cavity is 64 mm while the feed lines are approximately 126 mm.

Method of shrinkage measurement

5 A 30.5x30.5x0.32 cm (12"x 12"x 1/8") flat panel is molded in a highly polished chrome plated matched metal die mold in a 75 TON Queens Hydraulic press. The exact dimensions of the four sides of this mold are measured to the thousandths of a mm at room temperature. The exact length of the four sides of the flat molded panel is also determined to the thousandth of a mm. These measurements are substituted into the equation below:

$$\frac{a-b}{a} = \text{mm/mm (inch/inch) shrinkage}$$

mm/mm (inch/inch) shrinkage x 1000 = $\mu\text{m/mm}$ (mils/inch) shrinkage.

10 a = the sum of the lengths of the four sides of the mold.

b = the sum of the lengths of the four sides of the molded panel.

Procedure for MCR measurements

15 Surface evaluations of molded fiber reinforced plastic (FRP) parts were obtained as follows:

A Bendix Profilometer or microrecorder was used to determine the surface smoothness of 30.5x30.5 cm (12"x12") panels molded from the various SMC formulations. A diamond stylus connected to the Bendix Profilometer passes over the surface of the panels, measuring the hills and valleys. These recorded surface variations are averaged to give the MCR reading ($\mu\text{m/mm}$; micro inches/inch) recorded in the report.

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Example 1

Possible changes in shrinkage control (which normally correlates to surface appearance) by means of a low reinforcement LP-40A based critical shrinkage control test utilizing vinyl acetate monomer as the crosslinkable monomer additive was carried out as shown in Table I with different formulations. The results of these variations are shown in Table I as well as where it can be seen that vinyl acetate monomer improved the shrinkage control from 1.0 μm per mm (mils per inch) to 0.4 μm per mm (mils per inch) over a range of 1 to 5 parts per hundred to resin of vinyl acetate monomer.

30 In all of the tables all materials listed are parts by weight except for the fiberglass reinforcement, which is expressed as a weight percent of the total mix.

TABLE I
Critical BMC shrinkage control test

	(1)	(2)	(3)	(4)
35	60			
Freeman Stypol® 2955				
Bakelite® LP-40A	30			
40	—	1	3	5
Vinyl acetate				
Styrene	10			
Snowflake®	175			
45	4			
Zinc stearate				
TBPB	1.5			
Modifier M®	3.0			
50	10			
Glass, 6.35 mm (1/4") (wt. %)				
JM-308A				
Molded 149°C (300°F)/75 tons—				
3 minutes				
55	1.0	0.8	0.6	0.4
Shrinkage, $\mu\text{m/mm}$ (mils/inch)				

Example 2

Further tests were run on a similar formula shown in Table II. Monomers such as diallyl phthalate, methyl methacrylate, vinyl norbornene, vinyl stearate, and butyl vinyl ether were examined at levels of 2.75 and 5.5 parts per 100 of resin. In all cases except methyl methacrylate, which is known to react readily with the polyester/styrene materials, improvements in shrinkage control were observed. Particularly good results were observed with the vinyl norbornene and vinyl stearate.

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TABLE II
Bulk molding compound critical shrink evaluation using various unsaturated monomers as additives

Formulation (parts by weight)	1	2	3	4	5	6	7	8	9	10
NR-3929	52.25	→	→	→	→	→	→	→	→	→
Bakelite® LP-40A	40	→	→	→	→	→	→	→	→	→
P8Q*	100 ppm	→	→	→	→	→	→	→	→	→
Styrene	5	→	→	→	→	→	→	→	→	→
Diallyl phthalate	2.75	→	→	→	→	→	→	→	→	→
Methyl methacrylate	2.75	→	→	→	→	→	→	→	→	→
Vinyl norbornene	2.75	→	→	→	→	→	→	→	→	→
Vinyl stearate	2.75	→	→	→	→	→	→	→	→	→
Butyl vinyl ether	2.75	→	→	→	→	→	→	→	→	→
Snowflake®	150	→	→	→	→	→	→	→	→	→
TBFB	0.5	→	→	→	→	→	→	→	→	→
PCO (50%)	1.0	→	→	→	→	→	→	→	→	→
Zinc stearate	2	→	→	→	→	→	→	→	→	→
Bakelite® VR-3	2	→	→	→	→	→	→	→	→	→
Modifier M18	3	→	→	→	→	→	→	→	→	→
H ₂ O	0.05	→	→	→	→	→	→	→	→	→
JM-308A, 6.35 mm (1/4"), wt. %	10	→	→	→	→	→	→	→	→	→
Viscosity, mPa.s	7.2	8.0	4.8	19.4	12.0	→	→	→	→	→
1 day, 10 ⁴ mPa.s	→	→	→	→	→	→	→	→	→	→
2 days, 10 ⁴ mPa.s	→	→	→	→	→	→	→	→	→	→
3 days, 10 ⁴ mPa.s	49.2	46.4	42.4	→	→	→	→	→	→	→
4 days, 10 ⁴ mPa.s	→	→	→	→	→	→	→	→	→	→
Shrinkage μm/mm (mils/inch)	0.56	0.98	0.21	0	0	0	0.83	0.4	0.58	0
Scum on mold	→	→	→	→	→	→	→	→	→	→
Control	→	→	→	→	→	→	→	→	→	→

Comments

*Based on NR-3929

Example 3

Other bulk molding compound formulations were run with two other thermoplastic shrinkage control agents, Bakelite® LP-100 and LP-60 low profile additives to determine the effect of crosslinkable monomers on shrinkage control and pigmentability. These data are shown in Table III. In the LP-60 system (40% by weight solution of a polycaprolactone of about 5000 molecular weight end-capped with phthalic anhydride, described in US—A—3,668,178 incorporated herein by reference) vinyl stearate and butyl vinyl ether improved shrinkage control but not pigmentability. With LP-100 (40% solution of vinyl acetate copolymer in styrene), vinyl acetate, vinyl stearate, and butyl vinyl ether all improved shrinkage control. The butyl vinyl ether also improved pigmentability.

TABLE III
Pigmentability and shrinkage control of LP-60 and LP-100 BMC systems using various monomers

Run No.	1A	2	3	4	5	6	7	8	9	10
Formulation										
NR-3929	60									
LP-60	35									
LP-100				35						
Styrene	5									
Vinyl acetate				3	6					
Vinyl stearate		3				3	6			
Butyl vinyl ether			3					3	6	
Snowflake®	150									
TBPP®	1									
Zinc stearate	4									
Bakelite® LP-100 Part B (50% in styrene)				3						
CM-2215 Pigment	7									
Modifier M®	2.4									
JM-308A, 6.35 mm (1/4"), wt. %	15									
Viscosity, mPa.s	3.7			46.4	44.8	43.2	40.0	40.0	37.6	44.0
1 day, 10 ⁶ mPa.s	10.8	5.6	8.5							
2 days, 10 ⁶ mPa.s										
Physical properties										
Shrinkage, µm/mm (mils/inch)	0.42	0	0	0.71	0.42	0	+0.35	0	0.21	1.08
Pigmentation rating (1=best; 3=worst)	3	3	3	2	3	3	3	1	3	2

Example 4

Further tests were run using USS MR 13031 polyester resin. Monomers such as vinyl cyclohexene, bicyclononadiene, octene-1, octene-2, dimethyl maleate and dimethyl fumarate.

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TABLE IV

Run No.	1	2	3	4	5	6	7
<u>Formulation</u>							
USS MR 13031	65	65	65	65	65	65	65
LP-40A	35	35	35	35	35	35	35
TBPP	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Zinc stearate	2	2	2	2	2	2	2
VR-3	2	2	2	2	2	2	2
Vinyl cyclohexene	—	2.75	—	—	—	—	—
Bicyclononadiene	—	—	2.75	—	—	—	—
Octene-1	—	—	—	2.75	—	—	—
Octene-2	—	—	—	—	2.75	—	—
Dimethyl maleate	—	—	—	—	—	2.75	—
Diethyl fumarate	—	—	—	—	—	—	2.75
Modifier M ⁽¹⁾	3	3	3	3	3	3	3
6.35 mm (1/4") glass (wt. %)	10	10	10	10	10	10	10
Molding viscosity, Brookfield HBT-5X TF-5, 10 ⁶ mPa.s	25.1	24.0	22.0	24.0	23.6	21.6	22.4
Shrinkage, $\mu\text{m}/\text{mm}$ (mils/inch)	0.83	0.29	0.45	0.0	0.0	0.47	0.93

Molding conditions: 450 g/149°C (300°F)/3 minutes/75 tons

⁽¹⁾ MgO dispersion (33%).

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Example 5

Further tests were run using Freeman Stypol 40-2955 polyester resin and Diene 221 monomer.

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TABLE V

Run No.	1	2	3
<u>Formulation</u>			
5	Freeman Stypol® 40-2955	65	65
	LP-40A	35	35
	Diene 221	—	3
10	Snowflake®	150	150
	<i>t</i> -Butyl perbenzoate	1.5	1.5
	Zinc stearate	4	4
15	USS Modifier M®	3	3
	6.35 mm (1/4") glass (wt. %)	10	10
	Molding viscosity, 10 ⁶ mPa . s	35	32
20	Shrinkage, µm/mm (mils/inch)	1.04	0.3
	% H ₂ O Absorption		
	24 hrs.	—	0.41
25	7 days	—	1.03
			1.36

Molding parameters (30.5x30.5x0.25 cm) (12"x12"x0.1") 2 mins/149°C (300°F) 75 tons.

Example 6

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Sheet molding compound runs were also made with a polyester molding composition containing in addition vinyl acetate monomer. These formulations are depicted in Table IV. Surface appearance was rated visually on complex hood scoop moldings after coating with a high gloss black paint as described earlier. In every case the use of vinyl acetate monomer improved the surface appearance.

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TABLE VI
SMC Formulations

		1	2	3	4
5	USS-MR-13031	65	→		
	LP-40A	28	→		
	Vinyl acetate	—	1	2	4
10	Snowflake®	142	→		
	Bakelite® VR-3	2	→		
	Zinc stearate	2	→		
15	TBPB	0.75	→		
	PDO (50%)	1.50	→		
	"B" Side ⁽¹⁾	22.1	→		
20	OCF-951; weight % 1"	→ Approximately 28 →			
	Molding viscosity, 10 ⁶ mPa . s Brookfield HBT-5X/TF/5 cpm	20.0	24.0	19.6	18.4
25	Shrinkage, µm/mm (mils/inch)	0.0	0.0	0.0	0.0
	Painted hood scoop:				
	Surface rating ⁽²⁾				
30	800 g/141°C (285°F)/90 sec/69 bar (1000 psi)	2—	3+	—	2+
	800 g/149°C (300°F)/90 sec/69 bar (1000 psi)	3—3+	3+—4—	3+	4

⁽¹⁾ Based on (wt. %) Merck Maglite® A (MgO)-5, Bakelite® LP-85-50, Snowflake 42®, and PDI-1803-3 as a predispersion.

⁽²⁾ Highest number is best.

40 Example 7

Additional runs were made with vinyl acetate monomer on a transfer press for molding complex shapes. This is a chrome plated match metal die type mold. The formulations employed are shown in Table V together with viscosity and shrinkage results. The materials used are identified in Table VI. The profilometer evaluations of 10.16 cm (four inch) discs transfer molding runs are presented in Table VII. The lower number obtained for Run 1 using vinyl acetate vis-a-vis the Control clearly indicates the smoother surface obtained.

TABLE VII
Bulk molding compound
Critical shrink evaluation of various monomers in an acrylic thermoplastic formulation

Run No.	1	2	3	4	5	6	7	8	9	10	11	12	13
Formulation													
NR-3529	60												
P-701	40												
Vinyl acetate	—	2.75	—	—	—	—	—	5.5	—	—	—	—	—
Diallyl phthalate	—	—	2.75	—	—	—	—	—	5.5	—	—	—	—
Methyl methacrylate	—	—	—	2.75	—	—	—	—	—	5.5	—	—	—
Vinyl norbornene	—	—	—	—	2.75	—	—	—	—	—	5.5	—	—
Vinyl stearate	—	—	—	—	—	2.75	—	—	—	—	—	5.5	—
Butyl vinyl ether	—	—	—	—	—	—	2.75	—	—	—	—	—	5.5
Snowflake®	150												
TBPB	1.0												
Zinc stearate	4												
Modifier M®	2.5												
JM-308A, 1/4", wt. %	10												
Viscosity, 10 ⁵ mPa.s	16.0	13.6	7.2	21.2	17.6	18.4	16.0	21.6	15.2	15.2	9.6	12.8	8.0
1 day, 10 ⁵ mPa.s	—	—	15.2	—	—	—	—	—	—	—	21.2	20.8	21.6
2 days, 10 ⁵ mPa.s	—	—	—	—	—	—	—	—	—	—	—	—	—
Shrinkage, µm/mm (mils/inch)	1.9	1.7	1.6	2.0	1.19	1.13	1.3	1.5	1.4	2.0	0.	0	0.71

TABLE VIII

Description of materials

- Freeman Stypol® 2955. An unsaturated polyester resin from Freeman Chemical Company which is a high reactivity isophthalic acid modified resin containing approximately 35 weight percent of styrene monomer.
- Bakelite® LP-40A. A product of Union Carbide Corporation which is a copolymer of vinyl acetate and acrylic acid (40 weight percent) dissolved in styrene (60 weight percent).
- Snowflak®. A calcium carbonate filler sold by *Thompson-Weimann, Inc.* having a mean particle size of 5 microns.
- TBPP. *tert*-butylperbenzoate.
- Modifier M®. A 33 weight percent dispersion of magnesium oxide in an unsaturated polyester carrier vehicle sold by USS Chemicals/Polyester Unit.
- NR-3929. A high reactivity isophthalic acid modified unsaturated polyester resin containing approximately 35 weight percent of styrene and sold by Rockwell International.
- PBQ. Parabenzoquinone.
- PDO. A 50% dispersion of *tert*-butylperoxoate in dioctyl phthalate sold by the *Lucida Division* of Penwalt Corp.
- Bakelite® VR-3. A mixture of commercial fatty acids sold by Union Carbide Corporation.
- JM 308. A sized fiberglass reinforcement of 6.35 mm (1/4") length sold by Johns Manville Corp.
- CM-2015. A black pigment dispersion provided by Plasticolors, Inc.
- PPG-3029. A sized, chopped fiberglass reinforcement supplied by PPG Industries.
- Bakelite® LP-85. A 40 weight percent solution of poly(vinyl acetate) in styrene sold by the Union Carbide Corporation.
- P-701. A 33 weight percent solution in styrene of a methyl methacrylate based thermoplastic polymer sold by Rohm and Haas.
- NR-3529. An unsaturated polyester resin made by the condensation of 1.0 mole of maleic anhydride and 1.1 moles of propylene glycol and containing approximately 33 weight percent of styrene and manufactured by Rockwell International.
- MR-13031. A highly reactive unsaturated polyester resin believed to be *ortho*-phthalic anhydride modified containing approximately 40 weight percent of styrene sold by USS Chemicals Polyester Unit.
- OCF-951. A fiberglass roving chopped to desired length on the sheet molding compound machine and sold by Owens Corning Fiberglass Corp.
- Bakelite® LP-100 Part 8. A proprietary anionic surface active agent sold by Union Carbide Corporation.
- Camel Wite®. A finely divided calcium carbonate filler of average diameter size of 2.5 microns supplied by H. T. Campbell.
- PDI 1803. A black pigment dispersion sold by Pigment Dispersions, Inc.
- PG-9089. A thickener dispersion containing a ratio of 3.75 parts magnesium hydroxide and 1.0 parts of $\text{Ca}(\text{OH})_2$ at approximately 28 weight percent solids supplied by Plasticolors, Inc.
- Merck Marinc H®. A grade of magnesium hydroxide supplied by Merck and Company.
- Bakelite® LP-60. A 40 weight percent solution in styrene of a phthalic anhydride capped poly(caprolactone) polymer sold by Union Carbide.
- Bakelite® LP-100. A 40 weight percent solution in styrene of a proprietary vinyl acetate based polymer sold by Union Carbide.
- Diene 221.

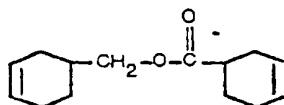


TABLE IX
Transfer molding runs

	Run	Control	1
5	USS MR-13031	60	60
	Bakelite® LP-40A	40	40
	Vinyl acetate	—	3
10	Camel Wite®	140	140
	ASP-400	21	21
	Zinc stearate	4	4
15	TBPB	1.5	1.5
	PBQ	0.02	0.02
	PDI 1803	0.3	0.3
20	PG 9089	20.0	20.0
	PPG-3029 (wt. %) 6.35 mm (1/4") fibers	20	20
25	Profilometer		
	MCR	50	31
	Tensile strength, N/mm ² (psi)	28.96 (4,200)	31.03 (4,500)

30 Example 8

35 The criticality of the upper level of the amount of secondary vinyl monomer used in this invention is demonstrated by the formulations and Control presented in Table VIII. It can be seen here that while 35 parts by weight of LP-40A alone affords cured surfaces with satisfactory surface ratings, the inclusion of the secondary vinyl monomers vinyl acetate and diallyl phthalate at a level of 21 parts produced cured surfaces with inferior ratings via-à-vis the Control.

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TABLE X
Evaluation of LPS-40A dissolved in vinyl acetate and diallyl phthalate

	Control	A	B
5			
	USS-13031	65	65
	LP-40A	35	35 LPS40A/VAc
	Snowflake®	150	150
10	TBFB	1.5	1.5
	Zinc stearate	4	4
	Modifier M®	2.2	2.2
15	OCF-951 wt. %	27.4	25.1
	Hood scoop painted surface rating		
20	69 bar (1000 psi)	3	2-
	34.5 bar (500 psi)	3+	2+
	Second monomer level (phr)	—	21

DAP=diallyl phthalate monomer.
VAc=vinyl acetate monomer.

LPS-40A is the vinyl acetate/acrylic acid copolymer thermoplastic dissolved (40%) in styrene (60%) to form LP-40A. In A above 40% LPS-40A is dissolved in 60% vinyl acetate monomer. In B above 40% LPS-40A is dissolved in 60% diallylphthalate.

Cure conditions for SMC were 800 g charge at 149°C (300°F) for 2 minutes at the molding pressure indicated.

Example 9

In order to distinguish the composition disclosed in US—A—3,830,875 from the claimed invention, Example 3 of US—A—3,830,875 and a comparative example were run as closely as possible to each other. In this reference the low profile additive used is a mixture of polystyrene and polyethylene. Repeating this Example using vinyl acetate as an additional monomer in the conventional polyester heat-curable composition, the surface values shown in Table IX were inferior to a composition where the vinyl acetate was omitted. This demonstrates that the use of vinyl acetate as a secondary vinyl monomer is only effective when used in the compositions of the instant invention.

TABLE XI

		Patent Example 3*	1
5	PPG-50239	154	
	Polystyrene in styrene (35%)	39	
10	Ionol	0.8	
	PDO (50%)	8	
	Zinc stearate	8	
15	Microthene® FN-510	23	
	Snowflake®	394	
	Vinyl acetate	15	None
20	Modifier M®	4.3	
	6.35 mm (1/4") fibers wt. %	16	
	Shrinkage control $\mu\text{m/mm}$ (mils/inch)	0.17	0.67
25	Profilometer MCR	61	49

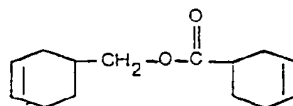
* Example from US—A—3,830,875, Example No. 3, Table 3a.

Claims

1. A method for producing low shrink molded articles with superior surface appearance from a sheet molding or bulk molding composition containing an unsaturated polyester, a polymerizable ethylenically unsaturated monomer which serves to crosslink the unsaturated polyester to a thermoset product and a thermoplastic vinyl acetate polymer low profile additive, characterized by incorporating into said composition a secondary crosslinkable vinyl monomer having a reactivity ratio with styrene of greater than 1 in an amount of from 1 to 10 parts per 100 parts of the total composition of polyester resin, thermoplastic polymer and monomer.

2. The method of claim 1 wherein the secondary vinyl monomer has a reactivity ratio with styrene of greater than 5, preferably greater than 20.

3. The method of claim 1 or 2 wherein the secondary vinyl monomer is vinyl acetate, or vinyl stearate, or vinyl norbornene, or dicyclopentadiene, or butyl vinyl ether, or diallyl phthalate, or has the formula:



4. The method of any of claims 1 to 3 wherein the composition additionally comprises a thickening agent such as magnesium oxide.

5. The method of any of claims 1 to 4 wherein the composition additionally comprises a reinforcing filler such as glass fiber.

6. The method of any of claims 1 to 5 wherein the composition additionally comprises a rubber or elastomer.

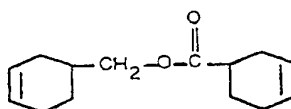
7. The method of any of claims 1 to 6 wherein the low profile additive is a carboxylated vinyl acetate polymer low profile additive.

8. A sheet molding and bulk molding composition containing an unsaturated polyester, a polymerizable

ethylenically unsaturated monomer which serves to crosslink the unsaturated polyester to a thermoset product and a thermoplastic vinyl acetate polymer low profile additive, characterized in that it comprises a secondary crosslinkable vinyl monomer having a reactivity ratio with styrene of greater than 1 in an amount of from 1 to 10 parts per 100 parts of the total composition of polyester resin, thermoplastic polymer and monomer and sufficient to provide a superior surface appearance of the molded articles produced.

9. The composition of claim 8 wherein the secondary vinyl monomer has a reactivity ratio with styrene of greater than 5, preferably greater than 20.

10. The composition of claim 8 or 9 wherein the secondary vinyl monomer is vinyl acetate, vinyl stearate, vinyl norbornene, dicyclopentadiene, or butyl vinyl ether, or diallyl phthalate, or has the formula:



11. The composition of any of claims 8 to 10 additionally comprising a thickening agent such as magnesium oxide.

12. The composition of any of claims 8 to 11 additionally comprising a reinforcing filler such as glass fiber.

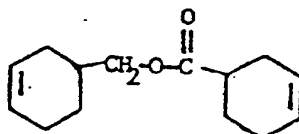
13. The composition of any of claims 8 to 12 additionally comprising a rubber or elastomer.

Patentansprüche

1. Verfahren zur Herstellung von Formkörpern mit niedriger Schrumpfung und überlegenem Oberflächenaussehen aus einer SMC- oder BMC-Formmasse, die einen ungesättigten Polyester, ein polymerisierbares, ethylenisch ungesättigtes Monomer, das zur Vernetzung des ungesättigten Polyesters zu einem hitzegehärteten Produkt dient, und ein thermoplastisches Vinylacetatpolymer als schrumpfungshemmenden Zusatz enthält, dadurch gekennzeichnet, dass man der Formmasse ein sekundäres vernetzbares Vinylmonomer, das ein Reaktivitätsverhältnis mit Styrol von grösser als 1 aufweist, in einer Menge von 1 bis 10 Teilen pro 100 Teile der Gesamtzusammensetzung von Polyesterharz, thermoplastischem Polymer und Monomer zusetzt.

2. Verfahren nach Anspruch 1, worin das sekundäre Vinylmonomer ein Reaktivitätsverhältnis mit Styrol von grösser als 5, vorzugsweise grösser als 20, aufweist.

3. Verfahren nach Anspruch 1 oder 2, worin das sekundäre Vinylmonomer Vinylacetat oder Vinylstearat oder Vinylnorbornen oder Dicyclopentadien oder Butylvinylether oder Diallylphthalat ist oder die Formel hat:



4. Verfahren nach irgendeinem der Ansprüche 1 bis 3, worin die Formmasse zusätzlich ein Verdickungsmittel, wie Magnesiumoxid, umfasst.

5. Verfahren nach irgendeinem der Ansprüche 1 bis 4, worin die Formmasse zusätzlich einen verstärkenden Füllstoff, z. B. Glasfasern, umfasst.

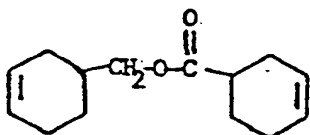
6. Verfahren nach irgendeinem der Ansprüche 1 bis 5, worin die Formmasse zusätzlich einen Kautschuk oder ein Elastomer umfasst.

7. Verfahren nach irgendeinem der Ansprüche 1 bis 6, worin der schrumpfungshemmende Zusatz ein carboxyliertes Vinylacetatpolymer ist.

8. SMC- und BMC-Formmasse, enthaltend einen ungesättigten Polyester, ein polymerisierbares, ethylenisch ungesättigtes Monomer, das zur Vernetzung des ungesättigten Polyesters zu einem hitzegehärteten Produkt dient, und ein thermoplastisches Vinylacetatpolymer als schrumpfungshemmenden Zusatz, dadurch gekennzeichnet, dass sie ein sekundäres vernetzbares Vinylmonomer mit einem Reaktivitätsverhältnis mit Styrol von grösser als 1 in einer Menge von 1 bis 10 Teilen pro 100 Teile der Gesamtzusammensetzung von Polyesterharz, thermoplastischem Harz und Monomer enthält, die ausreicht, um dem hergestellten Formkörper überlegenes Oberflächenaussehen zu verleihen.

9. Masse nach Anspruch 8, worin das sekundäre Vinylmonomer ein Reaktivitätsverhältnis mit Styrol von grösser als 5, vorzugsweise grösser als 20, aufweist.

10. Masse nach Anspruch 8 oder 9, worin das sekundäre Vinylmonomer Vinylacetat, Vinylstearat, Vinyl-norbornen, Dicyclopentadien oder Butylvinylether oder Diallylphthalat ist oder die Formel hat:



11. Masse nach irgendeinem der Ansprüche 8 bis 10, die zusätzlich ein Verdickungsmittel, wie Magnesiumoxid, umfasst.

12. Masse nach irgendeinem der Ansprüche 8 bis 11, die zusätzlich einen verstärkenden Füllstoff, z. B. Glasfasern, umfasst.

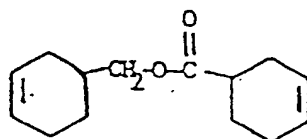
13. Masse nach irgendeinem der Ansprüche 8 bis 12, die zusätzlich einen Kautschuk oder ein Elastomer umfasst.

Revendications

1. Procédé de production d'articles moulés à faible retrait de très bon aspect superficiel, à partir d'une composition de moulage en feuille ou de moulage en masse contenant un polyester insaturé, un monomère à insaturation éthylénique polymérisable qui sert à la réticulation du polyester insaturé en un produit thermodurci, et, comme additif bas profil, un polymère d'acétate de vinyle thermoplastique, caractérisé par l'incorporation à ladite composition d'un monomère vinylique réticulable secondaire ayant un rapport de réactivité avec le styrène supérieur à 1 en une quantité de 1 à 10 parties pour 100 parties de la composition totale de résine polyester, de polymère thermoplastique et de monomère.

2. Procédé suivant la revendication 1, dans lequel le monomère vinylique secondaire a un rapport de réactivité avec le styrène supérieur 5 et de préférence supérieur à 20.

3. Procédé suivant la revendication 1 ou 2, dans lequel le monomère vinylique secondaire est l'acétate de vinyle ou le stéarate de vinyle ou le vinyl-norbornène ou le dicyclopentadiène ou l'éther de butyle et de vinyle ou le phthalate de diallyle ou répond à la formule :



4. Procédé suivant les revendications 1 à 3, dans lequel la composition comprend en outre un agent épaississant tel que l'oxyde de magnésium.

5. Procédé suivant l'une quelconque des revendications 1 à 4, dans lequel la composition comprend en outre une charge de renforcement telle que de la fibre de verre.

6. Procédé suivant l'une quelconque des revendications 1 à 5, dans lequel la composition comprend en outre un caoutchouc ou un élastomère.

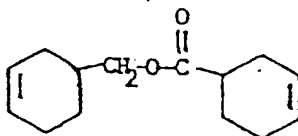
7. Procédé suivant l'une quelconque des revendications 1 à 6, dans lequel l'additif bas profil est un additif bas profil du type d'un polymère d'acétate de vinyle carboxylé.

8. Composition de moulage en feuille ou de moulage en masse contenant un polyester insaturé, un monomère à insaturation éthylénique polymérisable qui sert à la réticulation du polyester insaturé en un produit thermodurci, et comme additif bas profil un polymère d'acétate de vinyle thermoplastique, caractérisée en ce qu'elle comprend un monomère vinylique réticulable secondaire ayant un rapport de réactivité avec le styrène supérieur à 1, en une quantité de 1 à 10 parties pour 100 parties de la composition totale de résine polyester, de polymère thermoplastique et de monomère et suffisante pour que les articles moulés produits aient un très bon aspect de surface.

9. Composition suivant la revendication 8, dans laquelle le monomère vinylique secondaire a un rapport

de réactivité avec le styrène supérieur à 5 et de préférence supérieur à 20.

10. Composition suivant la revendication 8 ou 9, dans laquelle le monomère vinylique secondaire est l'acétate de vinyle, le stéarate de vinyle, le vinyl-norbornène, le dicyclopentadiène ou l'éther de butyle et de vinyle ou le phtalate de diallyle ou répond à la formule :



11. Composition suivant l'une quelconque des revendications 8 à 10, comprenant en outre un agent épaississant tel que l'oxyde de magnésium.

12. Composition suivant l'une quelconque des revendications 8 à 11, comprenant en outre une charge de renforcement telle que de la fibre de verre.

13. Composition suivant l'une quelconque des revendications 8 à 12, comprenant en outre un caoutchouc ou un élastomère.